Proceedings of the Technical Sessions, 40 (2024) 63-70
Institute of Physics, Sri Lanka

Enhancement of Photocurrent of TiO_2 Film as a Modified Photoanode of Dye Sensitized Solar Cell by Electrodeposited Copper in the TiO_2 Particle Space

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1. ABSTRACT

Copper insertion on a TiO_2 active layer is a viable way to enhance the performance of Dye-Sensitized Solar Cells (DSSCs). The TiO_2-Cu electrode, the counter electrode of C, the natural Sri Lankan Jaffna grape dye, and the KI/I_2 based electrolyte comprise the DSSC device used in this study. Cu particles were potentiostatically electrodeposited on TiO_2 electrode at -700 mV vs. SCE in an acetate bath containing an aqueous solution of 0.1 M sodium acetate and 0.01 M cupric acetate at room temperature. The incorporation of Cu particles increased the visible range light absorption in the TiO_2 layer significantly. It has also seen a reduction in internal resistance since of the copper coating. There was a significant increase in the photocurrent density (J_{SC}) from 308 μA/cm^2 to 501 μA/cm^2 with deposition of 4.75 μg mass of Cu in 10s. The efficiency also enhances from 0.07 to 0.10%. The photocurrent of the DSSC with Cu particles was increased by 62% when compared to the DSSC without Cu particles.

Key words Copper, DSSC, Electrodeposited, Photocurrent

2. INTRODUCTION

The world's fuel and energy crisis has become very concerning. The burning of fossil fuels currently provides most of the energy used in the world[1]. A global movement is currently underway to develop sustainable energy solutions to the world's energy crisis. Solar energy is the most sustainable energy source and has the potential to overtake fossil fuels as the primary energy source in the near future[2]. There are several generations is of solar cells that have been developed. The first generation is based on single- or polycrystalline silicon, the second generation based on thin films, and the third generation based on dye-sensitized solar cells (DSSC) [3]. Dye sensitized solar cells are among the most promising alternatives due to their reasonable photon to current conversion, the ability to be coated on a flexible substrate, inexpensive, and easy production[4].

Titanium dioxide (TiO_2) has been widely used in solar cells as an electron transport medium or as a light absorber. Earlier research studies using TiO_2 semiconductors

produced good efficiency results for DSSC, further work must be done to achieve DSSC with maximum and stable outcomes. Several studies have tried to improve the performance of the DSSC by adding different material to the TiO_2 layer. In DSSCs, the treatment of TiO_2 with a noble metal such as gold (Au), silver (Ag) has been documented to reduce the recombination of photogenerated electron–hole pairs and enhance charge transfer efficiency[5]. Researchers have been searching for better plasmonic dopants for the working electrode. Cu is a promising dopant because of its advanced properties, such as localized surface plasmon resonance (LSPR) effect, source abundance, low toxicity, and lower cost compared to noble metals.

There are several ways for inserting Cu on TiO_2 films, including electroplating, nanocomposite, hydrothermal, sputtering, and pulse plating[6]. In this study, a simple approach to increasing the efficiency of solar cells that use TiO_2 as an active material has been described, which combines a doctor blade method for depositing the TiO_2 layer with an electroplating process for growing copper particles on the space between the TiO_2 particles. The electron configuration of copper is such that there is one valence electron on the outer shell[6] and can make easy transitions because of its low orbital energy levels. Copper is often used in semiconductor insertion because of this. It has been reported that Cu particles were injected into the pores of a thin coating of titanium dioxide (TiO_2)[7]. In the DSSC, the interaction between Cu and TiO_2 plays an essential role for reducing electron recombination and increasing electron transportation. This study prepared and characterized solar cells based on TiO_2/Cu incorporation.

3. METHODOLOGY

3.1 Preparation of the photoanode

Indium Doped Tin Oxide (ITO) conducting glass sheets in the size of 2.5 cm × 2.5 cm were cleaned respectively by acetone and distilled water for 10 minutes in an ultrasonic bath and dried. The scotch tape was placed on each ITO side. Then TiO_2 paste was spread by the doctor blade method. TiO_2 applied glass sheets were sintered at 450 °C for 1.5 hours after tapes had been removed. Cu thin films formed on TiO_2 at -700 mV vs Ag/AgCl in a three-electrode electrochemical cell with an acetate solution of 0.1 M sodium acetate and 0.01 M cupric acetate. The deposition time was 10 seconds, and the electrodeposition process was conducted at room temperature. The deposition bath was continually agitated at 50 rpm with a magnetic stirrer. At the end of the electrodeposition process, a compact ITO/ TiO_2/Cu film was obtained. ITO/ TiO_2/Cu electrodes were embedded in dye for 24 hours. Using a binder clip, samples were removed and sandwiched between the counter electrode and an electrolyte solution. The entire extraction procedure was carried out in a dark area.

3.1 Extraction of natural dyes

Grapes were peeled, and the peels were placed in a mortar and crushed well to extract the dye without adding any solvent. The mixture was ground for 20 minutes, and then the mixture was filtered.

3.2 TiO_2 Paste preparation

The TiO_2 was prepared by mixing 0.3 g TiO_2 powder (Titanium (IV) dioxide) with 2.5 ml of Ethanol. Then, 1 drop of acetic acid was added to the paste. The mixture was stirred for 10 minutes.

3.3 Electrolyte preparation

A mixture of 0.123g I_2 and 0.82 g of KI powder was mixed with 10 ml of acetonitrile in a beaker. The solution was kept at room temperature for 10 hours to perform the redox reactions. The electrolyte solution was stored in a dark bottle. A carbon electrode was prepared by using soot from burning candles.

3.4 Characterization of the solar cell

UV – vis measurements were taken from PekinElmer UV/VIS Lambda 365. J-V measurements and controlled potential coulometry readings were taken using a Gammy series G 300 potentiostat operated by ELS300 software.

4. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of TiO_2 electrode (the wavelength of the X-ray radiation (Cu Kα = 0.100 nm). The 2θ peaks are located at 2θ = 17.85º (101), 25.83º (103), 26.38º (104), 26.93º (112), 33.14º (200), 36.88º(105), 37.84º (211). The phase can be determined to be either rutile or anatase using the XRD pattern. The TiO_2 anatase phase corresponds to the preferred orientation. The impurities combined with the TiO_2 sample can be responsible for some of the small peaks that are not indexable. The efficiency of the cell will decrease because of these impurities.

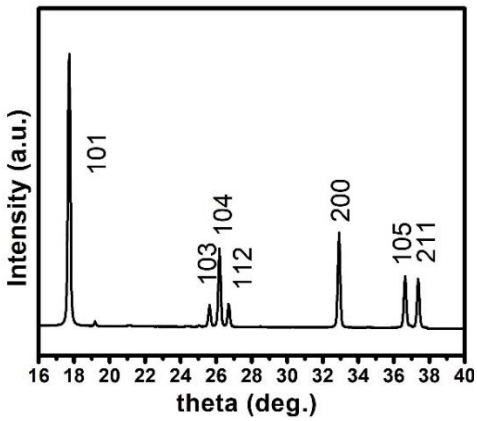


Figure 1: XRD patterns of TiO_2 photoelectrode used in DSSCs

The wavelength range of 300 to 900 nm, which included the UV and visible light spectrum, was used to measure the absorption spectrum of the sample. Figure 2 shows the absorbance spectrum of grape dye. The large absorption peak of the grape-dye is visible between 400 and 660 nm. Figure 3 shows the UV-absorption spectra of TiO_2 films without and with Cu particles. The absorbance has significantly increased in the absorption spectra of the TiO_2 film after the incorporation of Cu particles. This increase in absorption in the visible range due to the Cu particles may be more effective in increasing the photocurrent of the DSSCs.

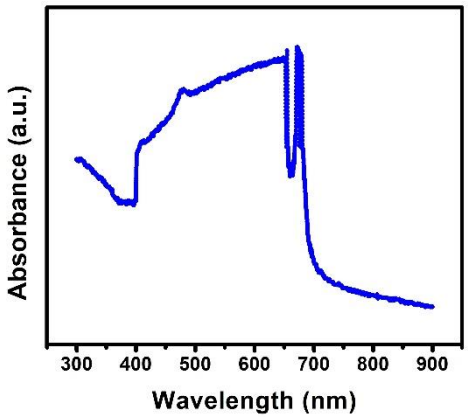


Figure 2: Absorbance spectrum for grape dye

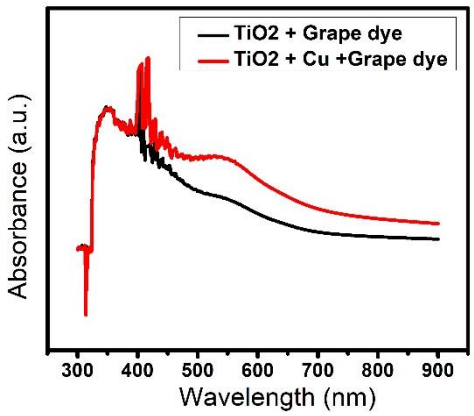


Figure 3: UV Spectrum of dye loaded TiO_2 fims with and without Cu

Internal resistances have a relationship to electron recombination and charge transfer in solar cells. High internal resistance reduces the performance of solar cells. Electrochemical Impedance Spectroscope (EIS) can be used to calculate internal resistance. The DSSCs have been shown to have three internal resistances: contact impedance (Z0), complex impedance of TiO_2/dye/electrolyte (Z2), diffusion impedance in the electrolyte (Z3), and counter electrode impedance (Z1)[7]. The most significant impedance Z contribution comes from Z2, which links incident photons to electron-hole recombination and regeneration. The internal resistance of DSSCs with and without a copper coating on the TiO_2 electrode is given in Table 1. The results obtained demonstrate

that copper on the TiO_2 thin film decreases the internal resistance. It reduces the rate of recombination and improves electron transport.

Table 1: Comparison internal resistances of DSSCs obtained by using EIS

DSSC	R_2 (Ω)	Total Resistance (Ω)
With Cu	65	65
Without Cu	87	87

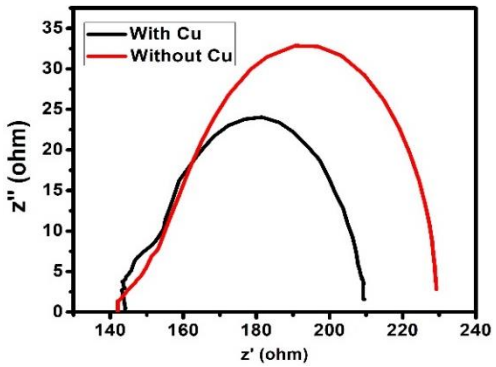


Figure 4: Nyquist plots of EIS spectra of DSSC with and without Cu particles

Table 2 shows controlled potential coulometry data of Cu deposition on TiO_2. This information can be used to compute how much Cu is deposited throughout the electrodeposition procedure.

Table 2: Cu mass on TiO_2 using exchange rate

Deposition time (s)	Exchanged Charge (C)	No. of Exchanged electrons ($\times 10^{17}$)	No of deposited Cu particles ($\times 10^{17}$)	Deposited Cu mass (μg)	Cu mass on TiO_2 (μg)	W/W % ($\times 10^3$)
10	0.032	2.00	1.00	10.55	4.75	0.124
20	0.052	3.24	1.62	17.01	7.65	0.201
30	0.069	4.31	2.16	22.79	10.26	0.270
40	0.086	5.37	2.7	28.49	12.82	0.337
50	0.103	6.43	3.2	33.76	15.20	0.339

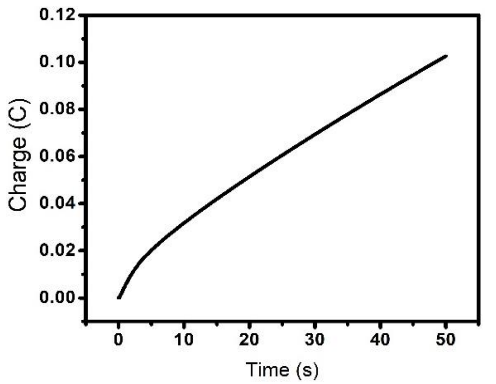


Figure 5: Controlled Potential Coulometry readings

Figure 6 shows the photovoltaic characteristics of DSSCs with Cu incorporation. The *J-V* characteristic is carried out on DSSC with insertion time variation of Cu on TiO_2. The large photocurrent density can be observed when deposition time is 10 s. The DSSC performance result is shown in Table 3. According to the data in Table 3, the highest efficiency is obtained for the electrodeposition time duration of 10 s.

Table 3: Photoactive performance of DSSCs at different insertion time

Deposition Time (s)	J_{SC} (μA/cm^2)	V_{OC} (V)	FF	η (%)
0	308	0.48	48	0.07
10	501	0.47	42	0.1
20	420	0.47	34	0.068
30	180.1	0.25	30	0.013
40	162.1	0.07	28	0.003
50	194.1	0.15	28	0.008

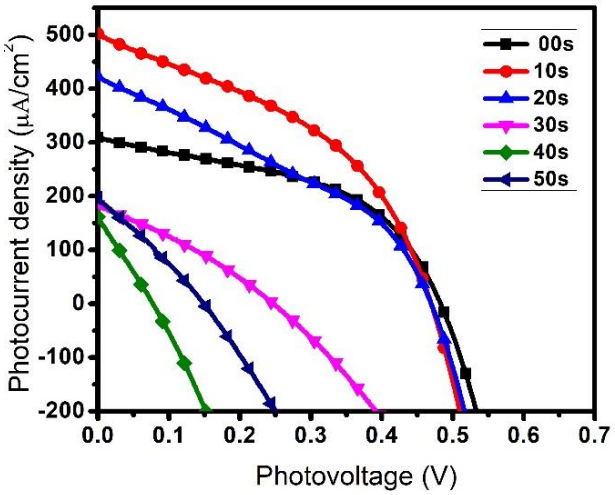
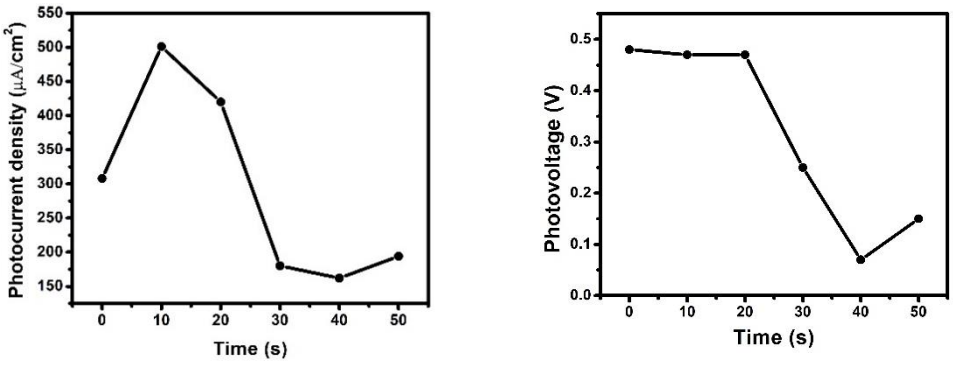


Figure 6: J – V characteristic curve of DSSCs with and without Cu particles at different insertion time



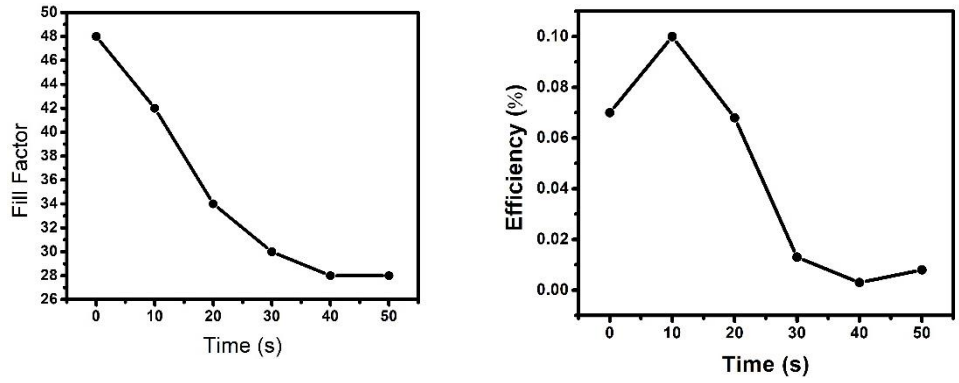


Figure 7: Variation of photoactive performance of DSSCs with different insertion time

The efficiency values obtained from DSSC decrease as Cu insertion time increases. A thicker Cu layer is inserted on the TiO_2 layer during large electrodeposition time and can cause to cover the entire TiO_2 layer. Cu decreases ability of TiO_2 to capture photons and transfer electrons, causing TiO_2 semiconductors to perform poorly[8].

Table 4: Comparison of the photovoltaic performance of DSSCs with and without Cu particles

	J_{SC} ($\mu A/cm^2$)	V_{OC} (V)	FF	η
TiO_2 + Grape dye	308	0.48	48	0.07 %
TiO_2 + Cu -10s + Grape dye	501	0.47	42	0.10 %

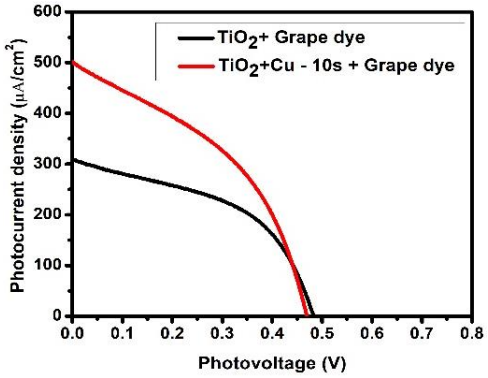


Figure 8: J – V characteristic curve of DSSCs with and without Cu particles.

5. CONCLUSION

The electrodeposition method was successfully used to deposit Cu particles on the TiO_2 layer. The addition of Cu particles resulted in a significant increase in the visible range light absorption in the TiO_2 layer. It has also been observed a decrease in internal resistance due to the copper coating. This might have had a significant impact in increasing the photocurrent of DSSC. In conclusion, the incorporation of Cu particles into DSSC on TiO_2 resulted in a 62% increase in photocurrent, which significantly raised the

efficiency from 0.07 to 0.10%. The maximum efficiency is obtained when the Cu insertion happens during the 10-second electroplating duration with deposition of 4.75 µg mass of Cu. A decrease in DSSC performance could result from excessive Cu insertion.

6. REFERENCES

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